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Wastes from Manufacture of Dyes and Pigments. Volume 9 Sulfur Dyes

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WASTES FROM MANUFACTURE OF DYES AND PIGMENTS: VOLUME 9. SULFUR DYES

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A preliminary study of the manufacture of sulfur dyes was conducted to determine if process waste streams might contain hazardous material. The study first identifies the dyes and pigments that belong to this segment of the industry, the amounts produced, and the known U.S. producers. The chemistry of these dyes is discussed as well as the overall production process and waste treatment practices. Several waste streams that could contain hazardous material are identified and two companies that produce representative dyes are recommended for a sampling program to confirm the composition and amounts of these waste streams.

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FOREWORD

When energy and material resources are extracted, processed, converted, and used, the related pollutional impacts on our environment and even on our health often require that new and increasingly more efficient pollution control methods be used. The Industrial Environmental Research Laboratory - Cincinnati (IERL-Ci) assists in developing and demonstrating new and improved methodologies that will meet these needs both efficiently and economically.

This report is one of a series of preliminary studies of segments of the dye and pigment manufacturing industry conducted for the Organic and Inorganic Chemicals and Products Branch of the Industrial Pollution Control Division. The objective of these studies was to determine if process waste streams might contain hazardous material and to recommend sites where a sampling program could be used to confirm the nature of any hazards that were identified.

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ABSTRACT

A preliminary study of the manufacture of sulfur dyes was conducted to determine if process waste streams might contain hazardous material. The study first identifies the dyes and pigments that belong to this segment of the industry, the amounts produced, and the known U.S. producers. The chemistry of these dyes and pigments is discussed as well as the overall production process and waste treatment practices. Several waste streams that could contain hazardous material are identified and two companies that produce representative dyes and pigments are recommended for a sampling program to confirm the composition and amounts of these waste streams.

This report is submitted in fulfillment of Contract No. 68-03-2944 by SRI International under the sponsonship of the U.S. Environmental Protection Agency. The report covers the period December 1981 to August 1982, and work was completed as of July 31, 1983.

CONTENTS

FOREWORD iii

ABSTRACT iv

TABLES vi

1. INTRODUCTION 1

2. SUMMARY AND CONCLUSIONS 5

3. PROCESS CHEMISTRY 6

   Introduction 6
   Sulfur Bake 7
   Polysulfide Bake 9
   Solvent Thionation 9

4. ORGANIC AND INORGANIC INTERMEDIATES AND REAGENTS IN SULFUR DYE PRODUCTION 12

5. SOURCES OF WASTE DISCHARGES DURING DYE AND PIGMENT MANUFACTURING 17

   Overview of Dye and Pigment Production Processes 17
   Material in the Waste Streams from Sulfur Dye Production 19

REFERENCES 25

TABLES

Number		Page
1.	Sulfur Dyes Included in This Study	3
2.	Organic Intermediates Used to Produce Sulfur Dyes	13
3.	Organic Reagents Used to Produce Sulfur Dyes	15
4.	Inorganic Reagents Used to Produce Sulfur Dyes	16
5.	Organic Materials that May Appear in the Waste Streams from the Production of Sulfur Dyes	21
6.	1979 Producers of Sulfur Dyes	24

SECTION 1

INTRODUCTION

The Resource Conservation and Recovery Act (RCRA) requires that hazardous solid wastes produced by manufacturing operations be identified and disposed in a manner that limits the release of hazardous materials to the environment. To date, many specific waste streams from manufacturing processes are listed in regulations as being hazardous because of their chemical composition. The objective of this study was to determine if wastes produced by the manufacture of dyes and pigments in the United States require listing as hazardous materials. An analysis of both the chemistry and the physical processing involved in the dye and pigment manufacturing is used to identify all wastes that may contain significant chemical hazards. An analysis of the industry is used to determine specific manufacturers where the candidate wastes may be produced. This information allows contractors of the U.S. Environmental Protection Agency to design a sampling and analysis program to confirm or disprove the presence of hazardous materials in the candidate wastes and thereby develop a basis for listing dye and pigment manufacturing wastes under RCRA. This report deals with the wastes produced from the manufacture of sulfur dyes.

Sulfur dyes have been produced commercially for more than 100 years. In spite of this long history and unlike most dyes of other classes that are clearly defined compounds of known structure, the sulfur dyes are, with few exceptions, mixtures of variable and unknown composition. There is disagreement as to what defines a sulfur dye. The early sulfur dyes formed a "chemical class" in that they were prepared from sulfurization or "thionation" of relatively simple intermediates with either sulfur or sodium polysulfide. They also formed a "dyeing class" in that as water-insoluble substances they were brought into soluble form for dyeing by treatment with a hot solution containing alkali and sodium sulfide. However, some newer dyes were introduced that were synthesized by a thionation procedure, but were dyed from an alkaline dithionate vat (sodium hydrosulfite vat) in the manner of vat dyes. Some argued that "sulfur dyes are best defined as those dyes which are applied in a reduced state from solutions containing sodium sulfide, hydrosulfide, or polysulfide, and which are subsequently oxidized on the fiber" (Orton, 1965). This definition precluded dyes made by a thionation procedure that were applied as vat dyes. However, in the listing of dyes by classes in the Colour Index (The Society of Dyers and Colourists, 1980), the "sulfurized vat dyes" are included in the sulfur dye chemical class. Therefore, we included these dyes in this study.

Table 1 gives the 1979 U.S. production data for the 36 commercially significant sulfur dyes included in this study--dyes produced at greater than 2.3 metric tons. Table 1 is arranged according to the Colour Index (C.I.) number (Colour Index, The Society of Dyers and Colourists, 1980). These 1979 U.S. production levels were taken from the the Organic Dyes and Pigments Data Base prepared by SRI International (Swett, et al., 1983). For all the dyes listed in Table 1, the production is shown only as an amount greater than a minimum number. This is because public sources do not list production values for dyes and pigments produced by fewer than three manufacturers or by three or more where one or two dominate the market. Two of the dyes listed in Table 1 are produced by two manufacturers; all the remaining sulfur dyes are made by only one manufacturer. There are only two U.S. manufacturers for the sulfur dyes listed in Table 1.

The total production volume of sulfur dyes is not known. In the mid-1960's, the U.S. production of sulfur dyes ranged from 8100 to 9100 metric tons per year, representing 7% to 8% of total dye production (U.S. Tariff Commission, 1965, 1967, and 1968). The importance of sulfur dyes as a commercial class has declined (Allen, 1971), although they are still in demand because of their moderately good properties and low cost. Thus, Table 1 probably significantly underestimates the total production of sulfur dyes.

In the following sections of this report the process chemistry of the sulfur dyes and sources of wastes during dye and pigment manufacture are discussed in detail.

Table 1

SULFUR DYES INCLUDED IN THIS STUDY

C.I. No.	C.I. Name	1979 U.S. Commercial Production (metric tons/yr)
53000	Leuco Sulfur Brown 1:1	> 2.3
53040	Leuco Sulfur Yellow 1	> 2.3
53050	Leuco Sulfur Orange 1	> 2.3
53055	Leuco Sulfur Brown 10	> 2.3
53185	Leuco Sulfur Black 1	> 2.3
53185	Sulfur Black 1	> 4.5
53186	Solubilised Sulfur Black 1	> 2.3
53190	Leuco Sulfur Black 10	> 2.3
53195	Leuco Sulfur Black 2	> 2.3
53195	Sulfur Black 2	> 2.3
53228	Sulfur Red 10	> 2.3
53228	Leuco Sulfur Red 10	> 2.3
53235	Leuco Sulfur Blue 11	> 2.3
53280	Leuco Sulfur Brown 31	> 2.3
53290	Leuco Sulfur Black 11	> 2.3
53290	Sulfur Black 11	> 2.3
53290	Leuco Sulfur Black 11:1	> 2.3
53320	Leuco Sulfur Brown 52	> 2.3
53430	Leuco Sulfur Blue 9	> 2.3
53440	Leuco Sulfur Blue 7	> 2.3
53450	Leuco Sulfur Blue 13	> 4.5
53570	Leuco Sulfur Green 3	> 2.3
53571	Leuco Sulfur Green 2	> 2.3
53630	Vat Blue 43	> 2.3
-	Leuco Sulfur Black 18	> 2.3
-	Leuco Sulfur Brown 3	> 2.3

Table 1 (Concluded)

C.I. No.	C.I. Name	1979 U.S. Commercial Production (metric tons/yr)
-	Leuco Sulfur Brown 37	> 2.3
-	Leuco Sulfur Brown 95	> 2.3
-	Leuco Sulfur Green 16	> 2.3
-	Leuco Sulfur Green 34	> 2.3
-	Leuco Sulfur Green 35	> 2.3
-	Leuco Sulfur Green 36	> 2.3
-	Leuco Sulfur Red 14	> 2.3
-	Leuco Sulfur Yellow 17	> 2.3
-	Leuco Sulfur Yellow 21	> 2.3
-	Leuco Sulfur Yellow 22	> 2.3

SECTION 2

SUMMARY AND CONCLUSIONS

In this preliminary study of sulfur dye production, several waste streams were identified that might contain hazardous materials:

- Discarded shipping containers. These would contain dye intermediates and reagents.
- Solid residues from process synthesis, distillation, and filtration. These would contain unreacted dye intermediates and reagents and reaction by-products.
- Gaseous emissions that may contain hydrogen sulfide.
- Process wastewater that may contain mother liquor from filtering operations. These are brines containing inorganic sulfur compounds and some organic compounds.
- Wastewater treatment solids. The solids may be contaminated with low levels of all of the dye intermediates as well as the dyes themselves and some reaction by-products.

Only two companies produce sulfur dyes. We recommend that sampling be conducted at both companies to determine the composition of the waste emissions:

Martin-Marietta Corp., Sodyeco Div.
American Cyanmid Co.

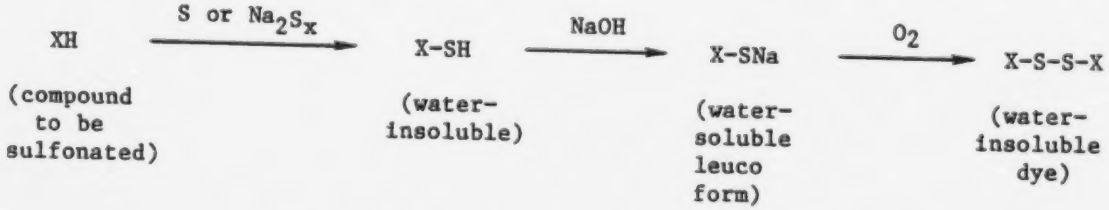
SECTION 3

PROCESS CHEMISTRY

INTRODUCTION

A discussion of the production of sulfur dyes is necessary to identify the emission sources and wastes that might be hazardous. This section focuses on the chemistry of the dye and pigment synthesis, with special attention given to the starting materials, intermediates, reaction conditions, and potential by-products.

Sulfur dyes are made by thionating relatively simple intermediates (such as aromatic amines, phenols, nitrophenols, and quinone imines) with sulfur or sodium polysulfide. Although sulfurization is a complex process, the reaction in its simplest form may be pictured as follows (Venkataraman, 1952):

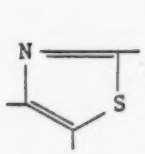


The products resulting from thionation are highly colored and water-insoluble. They are dissolved in solutions of sodium sulfide as a reduced or "leuco" form. The leuco form, X-SNa, is generally weakly colored, but has a strong affinity for cotton and other cellulosic fibers. On exposure to air or other oxidizing agents, a highly colored, water-insoluble product of high molecular weight is formed.

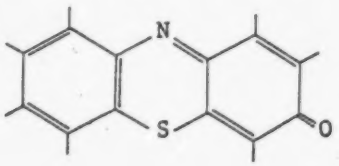
The sulfur dyes are amorphous and have no readily determined physical constants. They cannot be converted to well-characterized, closely related derivatives. It is also very difficult to purify a sulfur dye without altering the very physical and chemical properties that determine its commercial value. The sulfur dyes are mixtures of polymeric compounds of high molecular weight and, as commercially prepared, contain both organic and inorganic impurities.

According to Bigelow and Stallmann (1955), the sulfur content of the sulfur dyes is bound to the molecule in three different manners:

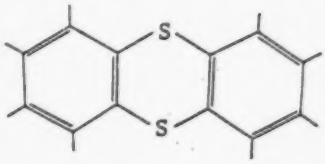
(1) It may exist as part of the basic chromophore as in the thiazole (I), the thiazone (II), or the thianthrene (III) group.



(I)



(II)



(III)

(2) Only a portion of the sulfur present in a typical sulfur dye is bound to the basic chromophore. Some of the remaining sulfur is attached to the aromatic rings in the form of disulfide or disulfoxide bridges. These linkages are broken on treatment with sodium sulfide with formation of -SNa groups, and on reoxidation the disulfide bridges are reformed on the fiber. The capacity of these groups to form intermolecular and intramolecular disulfide linkages is the determining factor in the high molecular weight of the sulfur dyes.

(3) Commercial sulfur dyes also contain large amounts of "loosely bound" sulfur. In the black sulfur dyes this amount of sulfur may account for 25% of the total sulfur content. This loosely bound sulfur is not removed by extraction with caustics or solvents, but is lost on repeated vatting and reoxidation or on prolonged oxidation with air. In certain dyes it is slowly oxidized to sulfuric acid on storage and may cause fabric dyed with these dyes to lose some of its original tensile strength.

Three general methods are used for producing sulfur dyes commercially: the sulfur bake, the polysulfide bake, and solvent thionation. Each is particularly adapted to certain intermediates and to manufacture of specific types of dyes. In all cases, hydrogen sulfide is evolved and is usually absorbed directly in sodium hydroxide solution to prevent health hazards (hydrogen sulfide is listed by the EPA as a hazardous material--toxic; Federal Register, 1980) and to recover the sulfur as sodium sulfide or hydrosulfide (Abrahart, 1977; Venkatarman, 1952).

SULFUR BAKE

In the sulfur bake process, sulfurization or thionation is brought about by heating and stirring a dry mixture of the organic material and sulfur. This technique is commonly applied to aromatic amines or diamines or their acylated derivatives and produces yellow, orange, and brown sulfur dyes. This is the cheapest method of producing sulfur dyes.

Sulfur bakes are generally performed in stationary iron kettles or in rotary bakers, which are heated by direct flame or by means of an oil jacket. In commercial practice (Bigelow and Stallman, 1955), the sulfur is usually melted in the kettle by itself. The intermediate is then added and the charge heated slowly to its final temperature, usually 200° to 250°C (however, for one of the sulfur dyes, C.I. Leuco Sulfur Brown 52, C.I. 53320, the final temperature is 350°C). Hydrogen sulfide is evolved and the reaction mass becomes increasingly viscous and finally solidifies. The reaction mixture is heated more until the required shade and strength is obtained. Increasing temperatures or time of reaction produces darker, stronger, and duller shades. Effective agitation of the mixture is necessary. However, local overheating is hard to avoid. This results in variations in the product quality and strength and requires careful blending for standardization.

When thionation is complete, the reaction mass is cooled somewhat and treated with aqueous sodium hydroxide to convert residual free sulfur into sodium sulfide and thiosulfate:

$$\underset{\text{Sodium hydroxide}}{6NaOH} + 4S \longrightarrow \underset{\text{Sodium sulfide}}{2\ Na_2S} + \underset{\text{Sodium thiosulfate}}{Na_2S_2O_3} + 3H_2O$$

When this is completed, the reaction mass is heated to evaporate the water. In the case of the cheaper sulfur dyes, standardization consists of grinding the powder and diluting with an inert material to standard tinctoral strength. Some of these cheaper dyes contain sufficient quantities of sodium sulfide to make them directly water soluble. However, other dry-baked sulfur colors contain too much unreacted starting material or insoluble partially charred by-products to permit a simple standardization. In these cases, the solution obtained by the addition of sodium hydroxide to the primary thionation mass is passed through a clarification press, and the sulfur color is isolated from the filtered liquor by evaporation on a drum dryer. Acidification of the clarified liquor can also be used to isolate the sulfur color. Acidification precipitates the dye in its leuco form; the product is then filtered, washed, and dried.

The following dyes from the list in Table 1 are reported to be made by the sulfur bake process (The Society of Dyers and Colourists, 1980):

C.I. 53040	Leuco Sulfur Yellow 1
C.I. 53050	Leuco Sulfur Orange 1
C.I. 53320	Leuco Sulfur Brown 52

POLYSULFIDE BAKE

This method differs from the sulfur bake only in that sodium polysulfide is used in place of free sulfur. It is widely used in the manufacture of brown, olive, and dull green sulfur dyes from aromatic amines, diamines, nitroamines, and phenols. The first commercially prepared sulfur dye, now known as C.I. Sulfur Brown 1 (C.I. 53000), is prepared by the polysulfide bake method using a variety of organic materials of animal or vegetable origin, such as coal or sawdust. The polysulfide bake tends to produce darker, stronger, and more soluble dyes than those that would be obtained from subjecting the same intermediates to a sulfur bake.

The sodium polysulfide used in the reaction is generally prepared by heating an aqueous solution of sodium sulfide and sulfur (Bigelow and Stallman, 1955; BIOS, 1945c):

$$Na_2S + nS \longrightarrow Na_2S_{(n+1)}$$

It can also be prepared by boiling aqueous sodium hydroxide with sulfur (Bigelow and Stallman, 1955):

$$6\ NaOH + (2n + 2)S \longrightarrow 2Na_2S_n + Na_2S_2O_3 + 3H_2O$$

When the sulfur is completely dissolved, the intermediate is added, and the reaction mixture is heated slowly to the final temperature ranging from 180° to 300°C, where it is maintained until the desired reaction is completed. Aqueous sodium hydroxide is then added to convert the residual sodium polysulfide to sodium sulfide. After this step, the entire reaction mass may be evaporated to dryness, or the aqueous solution may be clarified and the dye isolated by drum drying or by acidification and filtration, as mentioned previously.

The following dyes from the list in Table 1 are prepared using the polysulfide bake process (The Society of Dyers and Colourists, 1980; BIOS, 1945c):

C.I. 53000	Leuco Sulfur Brown 1:1
C.I. 53055	Leuco Sulfur Brown 10
C.I. 53280	Leuco Sulfur Brown 31

SOLVENT THIONATION

In solvent thionation the intermediate is treated with sodium polysulfide in liquid medium. The reaction mixture remains fluid throughout the

thionation, thereby permitting homogeneity to be obtained with good stirring and avoiding local overheating and charring. The intermediates used must be capable of reacting with sulfur readily at the low temperatures that result from solvent refluxing. Most commercial applications include the manufacture of sulfur colors from nitrophenols, indophenols, indamines, phenazines, and quinone imines.

Water is the most commonly used solvent; however, organic solvents are used when a dye of the highest purity and brightness is required or when the polysulfide ratio required is higher than can be maintained in water. The upper limit of stability of aqueous sodium polysulfide in boiling water can approximately be represented by the fomula $Na_2S_{4.5}$, whereas in organic solvents polysulfides represented by Na_2S_8 can easily be obtained (Bigelow and Stallman, 1955). Most of the commonly used solvents are alcohols, such as ethanol, butanol, and amyl alcohol. Cyclohexanol and mono ethers of aliphatic glycols are also used. Venkataraman (1952) reports that not only are the brightness and purity of the sulfurized vat dye Hydron Blue (C.I. Vat Blue 43, C.I. 53630) greatly improved by thionation in butanol solution, but the shade and dyeing properties are otherwise unobtainable.

In solvent thionation, the required amount of sulfur is completely dissolved in an aqueous or alcoholic solution of sodium sulfide or sodium hydroxide. The intermediates to be thionated are added, and the reaction proceeds under vigorous reflux. The temperature of reaction ranges from 85° to 130°C. At the end of thionation the reaction mass consists chiefly of the leuco form of the dye, partly dissolved and partly suspended in the reaction medium. Sodium hydroxide is added to the reaction mixture to convert the residual polysulfide to sodium sulfide. Any organic solvent used is distilled off and recovered.

The crude thionation product is sometimes precipitated from aqueous solution by the addition of salt. Polysulfide and other by-products are then removed by filtration and thorough washing of the filter cake with brine. More often, the aqueous mass is diluted with water, made alkaline by the addition of more sodium hydroxide, and oxidized by the passage of air through the suspension. During the air blowing, sodium thiosulfate is formed from the sodium disulfide present in the mixture:

$$2\ Na_2S_2 + 3O_2 \longrightarrow 2\ Na_2S_2O_3$$

Sodium disulfide — Sodium thiosulfate

The recovery of sodium thiosulfate from the mother liquors and its sale as a photography fixative is important in the competitive low prices of some of the sulfur dyes, especially C.I. Sulfur Black 1 (C.I. 53185). When all the sulfide is converted, the dye is precipitated in its oxidized form. The suspension is then filtered, washed, and dried.

Many sulfur dyes produced by solvent thionations are subjected to oxidative aftertreatments. The benefits of these treatments include the following:

- Brightening the shade of the dye
- Decreasing the content of free sulfur
- Improved and faster dyeing when applied to fibers.

This after-oxidation is usually performed by prolonging the aeration of the precipitated crude dye. Less commonly, the press cake of the leuco form of the dye may be suspended in water and treated with hydrogen peroxide, sodium perborate, or sodium hypochlorite.

The following sulfur dyes from Table 1 are produced by thionation in aqueous media:

C.I. 53185	Leuco Sulfur Black 1
C.I. 53185	Sulfur Black 1
C.I. 53186	Solubilized Sulfur Black 1
C.I. 53190	Leuco Sulfur Black 10
C.I. 53195	Leuco Sulfur Black 2
C.I. 53195	Sulfur Black 2
C.I. 53235	Leuco Sulfur Blue 11
C.I. 53440	Leuco Sulfur Blue 7
C.I. 53450	Leuco Sulfur Blue 13
C.I. 53570	Leuco Sulfur Green 3
C.I. 53571	Leuco Sulfur Green 2

The sulfur dyes from Table 1 that are produced by thionation in organic solvents are listed below with their corresponding solvent(s):

C.I. 53228	Leuco Sulfur Red 10 Sulfur Red 10	Cyclohexanol, ethylene glycol, or ethylene glycol monomethyl ether
C.I. 53290	Leuco Sulfur Black 11 Leuco Sulfur Black 11:1 Sulfur Black 11	Butanol
C.I. 53430	Leuco Sulfur Blue 9	Ethanol
C.I. 53630	Vat Blue 43	Butanol

SECTION 4

ORGANIC AND INORGANIC INTERMEDIATES AND REAGENTS IN SULFUR DYE PRODUCTION

Information on the organic and inorganic intermediates and reagents used to produce the sulfur dyes listed in Table 1 was compiled from information in the Colour Index (The Society of Dyers and Colourists, 1980), BIOS Reports (1945a-d), and Steadman et al. (1977). These sources provided information on the process chemistry of 24 of the sulfur dyes listed in Table 1. The remaining 12 sulfur dyes, which have no assigned Colour Index number, are of unknown chemical origin. Their process information is proprietary and unavailable through public sources.

Table 2 lists the organic intermediates, Table 3 lists the organic reagents, and Table 4 lists the inorganic reagents used in the production of sulfur dyes. Tables 2, 3, and 4 also identify those substances which, if present in solid waste streams, are subject to regulation as hazardous wastes under RCRA (Federal Register, 1980). The substances are identified by their RCRA hazard code.

Table 2

ORGANIC INTERMEDIATES USED TO PRODUCE SULFUR DYES

Organic Intermediates	Hazardous Waste Listing[a]
5-Amino-2-methylformanilide	
Aniline	I
_____,p-amino-N,N-dimethyl-	
_____,N,N-dimethyl-	
_____,p-nitroso-N,N-dimethyl-	
8-Anilino-5-(p-hydroxyanilino)-1-naphthalenesulfonic acid	
N-(p-Anilinophenyl)-p-quinone imine	
Bran	
Carbazole	
1-Chloro-2,4-dinitrobenzene	T
Coal	
Decacyclene (diacenaphtho[1,2-j;1′,2′-ℓ] fluoranthene)	
Diphenylamine	
Dithioacetoacetic acid, sodium salt	
Fats and fatty acids	
4,4′-Iminodiphenol	
Lignite	
2-Naphthol, sodium salt	
Oils	
Phenol	T
_____,p-amino-	
_____,2-amino-4,6-dinitro- (Picrimic acid)	
_____,p-(4-amino-m-toluidino)-	

Table 2 (Concluded)

Organic Intermediates	Hazardous Waste Listing[a]
Phenol,p-anilino-	
_____,p-(p-dimethylaminoanilino)-	
_____,2,4-dinitro-, and the sodium salt	T
_____,p-(2,4-dinitroanilino)-	
_____,p-2-naphthylamino-	
_____,p-nitro-	T
_____,p-nitroso-	
_____,2,4,6-trinitro (Picric acid)	
N-Phenyl-1-naphthylamine-8-sulfonic acid (N-Phenyl peri acid)	
Organic refuse	
Sawdust	
Sulfite cellulose waste liquors (free from calcium)	
Toluene, 2,4-diamino-	
o-Toluidine	

[a]Federal Register (1980), indicate the basis for EPA listing the material hazardous: Ignitable (I) and Toxic (T).

Table 3

ORGANIC REAGENTS USED TO PRODUCE SULFUR DYES

Organic Reagents	Hazardous Waste Listing[a]
Butyl alcohol	I
Cyclohexanol	
Ethyl alcohol	
Ethylene glycol	
Ethylene glycol monomethyl ether	

[a]Hazard codes from the Federal Register (1980), indicate the basis for EPA listing the material hazardous: Ignitable (I).

Table 4

INORGANIC REAGENTS USED TO PRODUCE SULFUR DYES

Copper sulfate
Hydrochloric acid
Hydrogen sulfide[a,b]
Iron (powder)
Iron oxide[a]
Sodium bicarbonate
Sodium bisulfite
Sodium carbonate
Sodium chloride
Sodium hydrosulfide
Sodium hydroxide
Sodium hypochlorite
Sodium nitrite
Sodium polysulfide
Sodium sulfide
Sodium tetrasulfide
Sodium thiosulfate[a]
Sulfur
Sulfuric acid

---

[a] By-products from the manufacturing process.

[b] Listed by the EPA as a toxic hazardous material (Federal Register, 1980).

SECTION 5

SOURCES OF WASTE DISCHARGES DURING DYE AND PIGMENT MANUFACTURING

The wide range of dye and pigment production processes and the specific plant characteristics and process control capabilities make estimation of material losses during dye manufacture a difficult task. In general, the most significant material losses are intermediates that do not react and by-products such as incomplete dye or pigment molecules. The intermediates and by-products from the dye manufacture are present either in the product or in the solid waste streams regulated under RCRA, which include wastewater, solid residue, and the vapor and dust emissions. The material in the wastewater is discharged in the plant effluent and some is discharged on any wastewater treatment solids.

OVERVIEW OF DYE AND PIGMENT PRODUCTION PROCESSES

Figure 1 illustrates the dye and pigment manufacturing process and shows where the losses of materials occur. The dye manufacturing equipment required to produce sulfur dyes consists of stationary reaction kettles (lead- or glass-lined, with heavy-duty agitators), rotary bakers (equipped with balls or rods for mixing), and standard filter presses, grinders, dryers, and blenders (Steadman et al., 1977; Bigelow and Stallman, 1955).

The dyes or pigments are usually produced in batches and the plants typically contain several reactor trains. Complex dyes may require use of several reactor trains.

Many of the sulfur dyes are produced in a single process operation in which the intermediate to be thionated is added to the molten sulfur or sodium polysulfide and baked at temperatures ranging from 100° to 350°C and for times ranging from 15 to 48 hours. Most of the sulfur dyes produced via the solvent thionation process require several process steps: formation of the intermediates followed by solvent reflux sulfurization.

For many years the sulfur dyes were sold as insoluble amorphous powders, which had to be pasted with water and dissolved with sodium sulfide for dyeing applications. These powders were unstable in storage: they oxidized in air and also were prone to spontaneous combustion. In the mid-1930s, prereduced solutions of the sulfur dyes were introduced. Orton (1969) reported that these prereduced liquids comprised 90% of the U.S. sulfur dye market. These liquid dyes are sold as "highly concentrated" solutions containing alkali and reducing agents for the dyeing application. The stability is much improved in

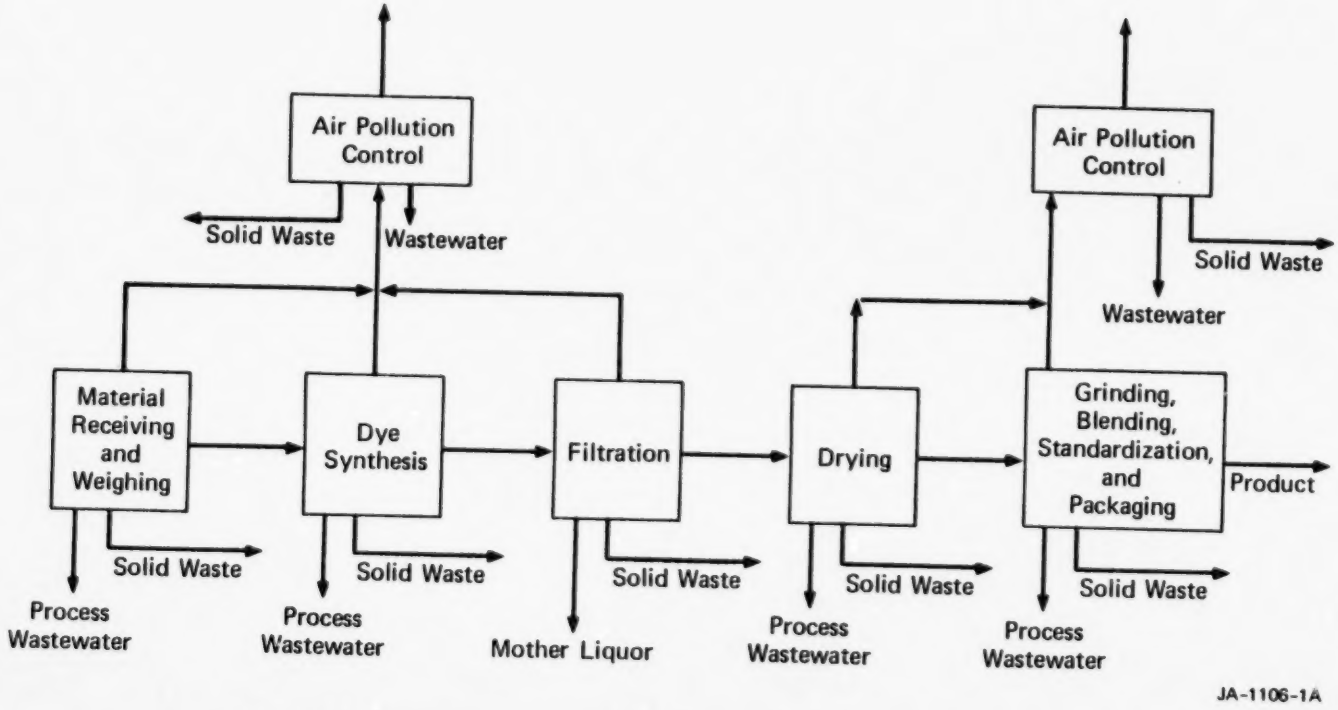


FIGURE 1 PRODUCTION OPERATIONS THAT ARE SOURCES OF WASTE EMISSIONS IN DYE AND PIGMENT MANUFACTURE

the liquid form, and the reducing agents protect the dye from atmospheric oxidation (Orton, 1969).

The sources of wastes from dye manufacture identified in Figure 1 are summarized below:

- Material handling--Air emissions from raw material dusting and volatilization, solid residue on shipping containers, and process wastewaters from equipment washdown.
- Dye syntheses--Air emissions from the volatilization of intermediates and by-products from reaction vessels, solid residuals from distillation residues and spills, and process wastewaters from equipment washdown.
- Product and intermediate filtration--Air emissions from unreacted intermediate and by-product volatilization during material handling, solid residues from spills, and process wastewater from equipment washdown. A significant additional source of process wastewater is the mother liquor when aqueous processes are used.
- Drying--Air emissions from volatilization of by-products and unreacted intermediates in the drying oven, and solid residues from spills and dusting of the product dye.
- Grinding, blending, standardization, and packaging--Solid residues from dusts produced by the grinding operations that may be either in the air streams from vent systems designed to prevent the material from entering the workplace environment or as a solid residue from spills.
- Air pollution control--Solid residues from baghouses or scrubbers collecting fine dusts and process wastewater from scrubbers.

MATERIAL IN THE WASTE STREAMS FROM SULFUR DYE PRODUCTION

Previous studies (Lapp et al., 1979; Bomberger and Boughton, 1983) have demonstrated that the major potential source of emissions is the process wastewater, primarily because it contains the mother liquor.

On the basis of the chemistry discussed in Section 3, these mother liquors, obtained from purifying the dyes, will probably contain unreacted intermediates, reaction by-products, unprecipitated dye or pigment, and salt. They may also contain mineral acids, such as sulfuric and hydrochloric acid.

Table 5 lists the sulfur dyes for which process chemistry information was available, identifying the intermediates and other organic chemicals used in the production. Table 5 does not identify process chemistry by-products that are likely to be present, for example, isomers of required intermediates and the reaction product of these with the other intermediates and reagents used in the process or the organic sulfur compounds that represent the intermediate

stages of thionation. The by-products were not included in this study because very little useful information dealing with the amount or nature of these by-products was found. The producers of the sulfur dyes are also indicated in Table 5. Table 6 lists all the producers of sulfur dyes in 1979 (with the associated letter codes used in Table 5) and the dyes they manufactured.

The most significant known hazardous material from the production of sulfur dyes is the hydrogen sulfide produced by thionation. This gaseous waste stream must be scrubbed effectively from the reactor effluent. The scrubbing operation, using sodium hydroxide, produces sodium sulfide, which can be recycled in the manufacturing process.

The solvent recovery operations may also lead to hazardous waste streams. For example, the spent solvent and the still bottoms from the recovery of n-butyl alcohol and isobutanol are considered hazardous materials (Federal Register, 1980).

Table 5

ORGANIC MATERIALS THAT MAY APPEAR IN THE WASTE STREAMS FROM THE PRODUCTION OF SULFUR DYES OF KNOWN MANUFACTURING PROCESS

1979 U.S. Commercial Producers	C.I. No.	C.I. Name	1979 U.S. Commercial Production (metric tons/yr)	Materials Released to the Environment
SDC	53000	Leuco Sulfur Brown 1:1	> 2.3	Leuco Sulfur Brown 1:1 Cellulose Source: brown coal organic refuse lignite sawdust bran sulfite cellulose waste liquors (free from calcium) oils fats and fatty acids
SDC	53040	Leuco Sulfur Yellow 1	> 2.3	Leuco Sulfur Yellow 1 5-Amino-2-methylformanilide Aniline
SDC	53050	Leuco Sulfur Orange 1	> 2.3	Leuco Sulfur Orange 1 2,4-Diaminotoluene
SDC	53055	Leuco Sulfur Brown 10	> 2.3	Leuco Sulfur Brown 10 2,4-Diaminotoluene
SDC	53185	Leuco Sulfur Black 1	> 2.3	Leuco Sulfur Black 1 1-Chloro-2,4-dinitrobenzene 2,4-Dinitrophenol 2,4-Dinitrophenol, sodium salt
ACY SDC	53185	Sulfur Black 1	> 4.5	Sulfur Black 1 1-Chloro-2,4-dinitrobenzene 2,4-Dinitrophenol 2,4-Dinitrophenol, sodium salt
SDC	53186	Solubilised Sulfur Black 1	> 2.3	Solubilised Sulfur Black 1 1-Chloro-2,4-dinitrobenzene 2,4-Dinitrophenol 2,4-Dinitrophenol, sodium salt
ACY	53190	Leuco Sulfur Black 10	> 2.3	Leuco Sulfur Black 10 p-Aminophenol 2,4-Dinitrophenol p-Nitrophenol p-Nitrosophenol
SDC	53195	Leuco Sulfur Black 2	> 2.3	Leuco Sulfur Black 2 2-Amino-4,6-dinitrophenol (Picrimic acid) 2,4-Dinitrophenol 2,4,6-Trinitrophenol (Picric acid)

Table 5 (Continued)

1979 U.S. Commercial Producers	C.I. No.	C.I. Name	1979 U.S. Commercial Production (metric tons/yr)	Materials Released to the Environment
SDC	53195	Sulfur Black 2	> 2.3	Sulfur Black 2 2-Amino-4,6-dinitrophenol (Picrimic acid) 2,4-Dinitrophenol 2,4,6-Trinitrophenol (Picric acid)
SDC	53228	Leuco Sulfur Red 10	> 2.3	Leuco Sulfur Red 10 p-Anilinophenol Cyclohexanol Ethylene glycol Ethylene glycol monomethyl ether
SDC	53228	Sulfur Red 10	> 2.3	Sulfur Red 10 p-Anilinophenol Cyclohexanol Ethylene glycol Ethylene glycol monomethyl ether
SDC	53235	Leuco Sulfur Blue 11	> 2.3	Leuco Sulfur Blue 11 p-(2,4-Dinitroanilino)phenol Dithioacetoacetic acid, sodium salt
SDC	53280	Leuco Sulfur Brown 31	> 2.3	Leuco Sulfur Brown 31 2-Naphthol, sodium salt
SDC	53290	Leuco Sulfur Black 11	> 2.3	Leuco Sulfur Black 11 Butanol 4,4′-Iminodiphenol p-2-Naphthylaminophenol Phenol
SDC	53290	Leuco Sulfur Black 11:1	> 2.3	Leuco Sulfur Black 11:1 Butanol 4,4′-Iminodiphenol p-2-Naphthylaminophenol Phenol
SDC	53290	Sulfur Black 11	> 2.3	Sulfur Black 11 Butanol 4,4′-Iminodiphenol p-2-Naphthylaminophenol Phenol
SDC	53320	Leuco Sulfur Brown 52	> 2.3	Leuco Sulfur Brown 52 Decacyclene

Table 5 (Concluded)

1979 U.S. Commercial Producers	C.I. No.	C.I. Name	1979 U.S. Commercial Production (metric tons/yr)	Materials Released to the Environment
SDC	53430	Leuco Sulfur Blue 9	> 2.3	Leuco Sulfur Blue 9 p-Amino-N,N-dimethylaniline p-(p-Dimethylaminoanilino)phenol N-N-Dimethylaniline Ethanol p-Nitroso-N,N-dimethylaniline hydrochloride Phenol
SDC	53440	Leuco Sulfur Blue 7	> 2.3	Leuco Sulfur Blue 7 p-(4-Amino-m-toluidino)phenol p-Nitrosophenol o-Toluidine
ACY SDC	53450	Leuco Sulfur Blue 13	> 4.5	Leuco Sulfur Blue 13 N-(p-Anilinophenyl)-p-quinone imine Diphenylamine p-Nitrosophenol
SDC	53570	Leuco Sulfur Green 3	> 2.3	Leuco Sulfur Green 3 p-Aminophenol 8-Anilino-5-(p-hydroxyanilino)-1-naphthalene sulfonic acid N-Phenyl-1-naphthylamine-8-sulfonic acid (N-Phenyl peri acid)
SDC	53571	Leuco Sulfur Green 2	> 2.3	Leuco Sulfur Green 2 p-Aminophenol 8-Anilino-5-(p-hydroxyanilino)-1-naphthalenesulfonic acid N-Phenyl-1-naphthylamine-8-sulfonic acid (N-Phenyl peri acid)
SDC	53630	Vat Blue 43	> 2.3	Vat Blue 43 Butanol Carbazole p-Nitrosophenol Phenol

Table 6

1979 PRODUCERS OF SULFUR DYES

C.I. No.	C.I. Name
American Cyanamid Co. (ACY)	
53185	Sulfur Black 1
53190	Leuco Sulfur Black 10
53450	Leuco Sulfur Blue 13
Martin-Marietta Corp., Sodyeco Div. (SDC)	
53000	Leuco Sulfur Borwn 1:1
53040	Leuco Sulfur Yellow 1
53050	Leuco Sulfur Orange 1
53055	Leuco Sulfur Brown 10
53185	Leuco Sulfur Black 1
53185	Sulfur Black 1
53186	Solubilised Sulfur Black 1
53195	Leuco Sulfur Black 2
53195	Sulfur Black 2
53228	Sulfur Red 10
53228	Leuco Sulfur Red 10
53235	Leuco Sulfur Blue 11
53280	Leuco Sulfur Brown 31
53290	Leuco Sulfur Black 11
53290	Leuco Sulfur Black 11:1
53290	Sulfur Black 11
53320	Leuco Sulfur Brown 52
53430	Leuco Sulfur Blue 9
53440	Leuco Sulfur Blue 7
53450	Lueco Sulfur Blue 13
Martin-Marietta Crop., Sodyeco Div. (SDC) (cont'd.)	
53570	Leuco Sulfur Green 3
53571	Leuco Sulfur Green 2
53630	Vat Blue 43
-	Leuco Sulfur Black 18
-	Leuco Sulfur Brown 3
-	Leuco Sulfur Brown 37
-	Leuco Sulfur Brown 95
-	Leuco Sulfur Green 16
-	Leuco Sulfur Green 34
-	Leuco Sulfur Green 35
-	Leuco Sulfur Green 36
-	Leuco Sulfur Red 14
-	Leuco Sulfur Yellow 17
-	Leuco Sulfur Yellow 21
-	Leuco Sulfur Yellow 22

REFERENCES

Abrahart, E. N., 1977. Dyes and Their Intermediates. Chemical Publishing Co., Inc., New York.

Allen, R.L.M. 1971. Colour Chemistry. Appleton-Century-Crofts, New York.

Bigelow, N. M., and O. Stallman. 1955. Sulfur Dyes. Chapter 6 in: The Chemistry of Synthetic Dyes and Pigments, H. A. Lubs, editor, Reinhold Publishing Corporation, New York.

BIOS (British Intelligence Objectives Subcommittee). 1945a. Infra-Red Reflectance of Coloured Textiles and Other Materials (Part I) and Dyes, Intermediates and Pharmaceutical Processes (Part II). Miscellaneous Report No. 55, H. M. Stationery Office, London.

BIOS (British Intelligence Objectives Subcommittee). 1945b. I.G. Farbenindustrie A.G. Manufacture of Intermediates for Dyestuffs at Griesheim, Hoechst, Ludwigshafen, Mainkur and Offenbach. (Part I and Part II). Final Report No. 986, H. M. Stationery Office, London.

BIOS (British Intelligence Objectives Subcommittee). 1945c. I.G. Farbenindustrie A.G. Manufacture of Sulfur Dyestuffs and Their Intermediates at Mainkur. Final Report No. 1155, H. M. Stationery Office, London.

BIOS (British Intelligence Objectives Subcommittee). 1945d. I.G. Farbenindustrie A.G. Manufacture of Thioindigoid and Sulfur Dyestuffs at Hoechst and Mainkur. Final Report No. 983, H. M. Stationery Office, London.

Bomberger, D. C., and R. L. Boughton. 1983. Wastes from Manufacture of Dyes and Pigments (Benzidine and Its Congeners Subsector). U.S. Environmental Protection Agency, Office of Research and Development, Industrial Environmental Research Laboratory, Cincinnati, Ohio. Contract No. 68-03-2934.

Federal Register. 1980. Identifications and Listing of Hazardous Waste. 45(98): 33119-33133 (May 19, 1980).

Lapp, T. W., T. L. Ferguson, H. Gadberry, F. Hoffmeister, F. Hopkins, and B. Thompson. 1979. A Preliminary Materials Balance for Dyes and Pigments from Benzidine and Three Benzidine Derivatives. Midwest Research Institute Draft Report for the U.S. Environmental Protection Agency, Office of Toxic Substances, Washington, D.C.

Orton, D. G. 1969. Sulfur Dyes. In: Kirk-Othmer Encyclopedia of Chemical Technology, Interscience, New York.

The Society of Dyers and Colourists. 1980. Colour Index. Lund Humphries Printers, London, England, Volumes 1-3, Third Edition, 1971; Volume 6, Revised Third Edition, 1975, Additions and Amendments Numbers 13-36, October 1974-July 1980.

Steadman, T. R., E. W. Helper, T. Parsons, G. E. Wilkins, and N. R. Phillips. 1977. Industrial Process Profiles for Environmental Use: Chapter 7. Organic Dyes and Pigments Industry. U.S. NTIS PB281479. EPA 600/2-77-023g. U.S. Environmental Research Laboratory, Cincinnati, Ohio.

Swett, L., A. Twhigg, and K. E. McCaleb. 1983. The Organic Dyes and Pigments Data Base. U.S. Environmental Protection Agency, Office of Research and Development, Industrial Environmental Research Laboratory, Cincinnati, Ohio. EPA Contract No. 68-03-2944.

U.S. Tariff Commission. 1965. Synthetic Organic Chemicals, U.S. Production and Sales, 1964. TC Publication 167, U.S. Government Printing Office, Washington, D.C.

U.S. Tariff Commission. 1967. Synthetic Organic Chemicals, U.S. Production and Sales, 1965. TC Publication 206, U.S. Government Printing Office, Washington, D.C.

U.S. Tariff Commission. 1968. Synthetic Organic Chemicals, U.S. Production and Sales, 1966. TC Publication 248, U.S. Government Printing Office, Washington, D.C.

Venkataraman, K. 1952. The Chemistry of Synthetic Dyes. Volume II. Academic Press Inc., Publishers, New York.